

A Novel Conjugated Polyelectrolyte: a Facile Synthetic Method for Poly(propynyltriphenylphosphonium bromide) using Transition Metal Catalysts

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A novel conjugated polyelectrolyte, poly(propynyltriphenylphosphonium bromide) has been synthesised using transition metal catalysts in quantitative yield.

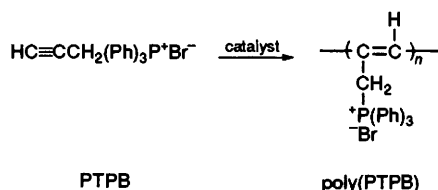
The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of linear conjugated polymers.¹ However, methods for the synthesis of polyelectrolytes having conjugated backbones are scarce and are mainly restricted to the following cases: the solid-state polymerization of propiolic salts by γ -irradiation,² water-soluble polyene polymers by quarterization of poly(6-bromo-hex-1-yne)³ and the synthesis of mono- and di-substituted ionic polyacetylenes by the activation of the acetylene bond, by strong electron-withdrawing substituents, in ethynylpyridine.⁴

Owing to their extensive conjugation and ionic nature, these polymers have potential for use as materials for mixed ionic and electronic conductivity, and energy storage devices such as batteries and permselective membrane.

In recent years, novel conjugated ionic polyelectrolytes have been synthesized by the cyclopolymerization of dihexyldipropynyl ammonium salts, having bromide and tosylate as counteranions, in the presence of metathesis catalysts.

Now we report the synthesis of a novel conjugated polyelectrolyte by solid-state polymerization of the monosubstituted phosphonium salt, propynyltriphenylphosphonium bromide (PTPB) using Mo- and W-based catalysts.

Table 1 shows the results for the polymerization of PTPB by Mo- and W-based catalysts. In most cases, the polymer yield was quantitative. Interestingly the acetylenic salt monomer having a bulky substituent was easily polymerized. As PTPB is mainly insoluble in the polymerization solvent (chlorobenzene), the polymerization seemed to be proceeded by a heterogeneous phase (solid-state) before a viscous oily phase was formed at the bottom of reaction ampule (polymerization temperature 90 °C).



The inherent viscosities were in the range 0.032–0.067. These low viscosities indicate that the molecular masses of the resulting poly(PTPB) were very low. It was deduced that the reason for the low molecular mass was that the monomer is a salt and polymerization proceeds in the solid-state because of the poor solubility of PTPB in chlorobenzene. Similar polymers obtained from dihexyldipropynyl ammonium salts were also found to have a low molecular mass.⁵

The initial purple colour of the MoCl₅ and WCl₆ catalyst solution disappeared as soon as the catalyst solution was injected into the PTPB-containing polymerization solvent. At the moment the polymerization mechanism of the acetylenic salt monomer by Mo- and W-based catalysts has not been elucidated. It was deduced that the polymerization of the acetylenic salt monomer may proceed by a different mechanism from the classical mechanism of metathesis polymerization. The resulting poly(PTPB)s were dark-brown powders and soluble in polar solvents such as methanol, DMF, Me₂SO, acetone, formic acid, nitrobenzene and chloroform, but insoluble in nonpolar aromatic and hydrocarbon solvents such as chlorobenzene, toluene, benzene, CCl₄, *n*-hexane *etc.*

In the ¹H NMR spectrum of poly(PTPB), as polymerization proceeded, the acetylenic proton peaks of PTPB at δ 1.8 disappeared; the broad peaks due to the protons on the conjugated double bonds and aromatic protons were observed at δ 7–8. In addition, the methylene peak was observed at *ca.* δ 2.55. The integration ratio of methylene protons/vinyl and aromatic protons was 0.11 [the calculated integration ratio of ideal poly(PTPB) = 0.125]. The ¹³C NMR spectrum of poly(PTPB) did not show the acetylenic carbon peaks (δ 70–80), instead the C=C bond peaks and aromatic carbon peaks were observed at δ 115–136. The IR spectrum of poly(PTPB) showed neither the acetylenic hydrogen stretching frequency (3151 cm⁻¹) nor the C=C bond stretching frequency (2110 cm⁻¹) present in the IR spectrum of PTPB. Instead, the C=C bond stretching frequency at 1612 cm⁻¹ indicated a conjugated unsaturation. The UV-VIS spectrum of poly(PTPB) exhibited the characteristic broad absorption peak at 400–550 nm which originated from the $\pi \rightarrow \pi^*$ transition of the conjugated polyene, this was not observed above 400 nm in the UV-VIS spectrum of PTPB. Thus, the spectral data indicated that the synthesised poly(PTPB) had a conjugated polyene backbone structure with pendant bulky methylene triphenylphosphonium bromide groups.

Table 1 Polymerization of PTPB by various transition metal catalysts^a

Entry	Catalyst system ^b (mol ratio)	M : M ^c	Polymer yield ^d (%)	η_{inh} ^e
1	MoCl ₅	50	97	0.035
2	MoCl ₅	100	99	0.051
3	MoCl ₅ -Ph ₄ Sn (1 : 1)	50	100	0.067
4	MoCl ₅ -EtAlCl ₂ (1 : 2)	50	100	0.050
5	WCl ₆	50	100	0.032
6	WCl ₆ -EtAlCl ₂ (1 : 2)	50	100	0.048

^a Polymerization was carried out at 90 °C for 48 h in chlorobenzene. Initial monomer concentration ($[M]_0$) was 0.5 mol dm⁻³. ^b Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before use. ^c Monomer : catalyst mol ratio. ^d *n*-Hexane-insoluble polymer. ^e Measured at a concentration of 0.5 g dl⁻¹ in methanol at 25 °C.

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